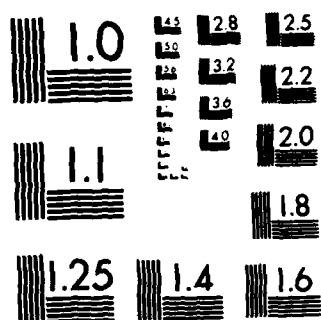


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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 83 - 0234	2. GOVT ACCESSION NO. AD A127029	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Development of Practical MO Techniques for Prediction of the Properties and Behavior of Materials		5. TYPE OF REPORT & PERIOD COVERED Final Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Michael J. S. Dewar		8. CONTRACT OR GRANT NUMBER(s) AFOSR-79-0008
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Texas at Austin Department of Chemistry Austin, TX 78712		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/B2
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NC Bolling AFB, DC 20332		12. REPORT DATE <i>Oct 82</i>
		13. NUMBER OF PAGES 40
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) SCF MO MNDO AMI		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) SEE OTHER SIDE		

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MICHAEL J.S. DEWAR

FINAL SCIENTIFIC REPORT

GRANT AFOSR 79-0008

NOVEMBER 1, 1979 - OCTOBER 31, 1982

DEVELOPMENT OF PRACTICAL MO TECHNIQUES
FOR PREDICTION OF THE PROPERTIES AND
BEHAVIOR OF MATERIALS

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ABSTRACT

Chemical Physics Division

A new parametric SCF MO method (AM1) has been developed which seems to have overcome the remaining deficiencies of MINDO/3 and MNDO, in particular their failure to reproduce hydrogen bonds, overestimation of nonbonded repulsions, and poor results for compounds containing nitrogen and oxygen, in particular those containing the NO₂ group. MNDO parameters have been devised for bromine and iodine. d-AOs have been introduced into MNDO and the resulting treatment (MNDOD) parameters for P and S. This work has been suspended to take advantage of AM1. Our programs have been rewritten, improved, and combined into a single package (MOPAC) which we will be sending to QCPE. The new programs run nearly three times faster.

INTRODUCTION

Unexpected practical problems interfered with the project supported by this grant during the first part of the grant period. I had obtained a grant from the National Science Foundation, with matching funds from the University of Texas, to acquire a Digital VAX 11-780 computer for my theoretical work. Due to delay by the University in providing their contribution, the computer was not ordered for nearly a year after I had obtained the grant. Since the CDC 6600 computer at the University of Texas Computation Center had become grossly overloaded, my research program was brought to a standstill. Worse still, just before the VAX was finally installed, the University replaced the CDC 6600 by a CYBER 750/760 dual computer. Since the computation center, rather unwisely, wrote their own operating system for this (as they had done with the 6600) and since it took them several months to get it properly functioning, we were left in the situation of having to rewrite our programs for two different computers at the same time without any reference as an aid in debugging them. However, in spite of these obstacles, satisfactory progress has been made in a number of areas.

DEVELOPMENTS IN TECHNIQUE

The most notable result during the current grant period, as during the first, has been the development of a new parametric procedure. MINDO/3 and MNDO suffer from certain specific weaknesses that limit their range of applicability, in particular inability to reproduce

hydrogen bonds, overestimation of interatomic repulsions that lead to too positive energies for crowded molecules (e.g. neopentane) and activation energies for reactions that tend to be too large, and too negative energies for small rings. MNDO also gave poor results for compounds containing the NO₂ group which made it unsatisfactory for studies of explosives. All these problems have been overcome in the new "third generation" treatment, which we are calling Austin Molecular Model 1 (AM1). AM1 is currently undergoing final tests and tuning, to make sure that it is in its optimum form before we extend it to other elements. The initial parametrization is for the "organic" elements (C,H,N,O).

In the meantime MNDO has been parametrized for bromine[6] and iodine[2], in response to requests from many organic chemists, and also for aluminum[3]. Papers[4,5] reporting results and parameters for sulfur and chlorine are also in press. We have also introduced d AOs into MNDO and parametrized the resulting treatment (MNDOD) for sulfur and phosphorus. A preliminary parametrization for chromium was also carried to a point where success seemed assured. Further work in this area has naturally been suspended awaiting the finalization of AM1.

Technical developments during the current grant period have led to major improvements in our computer programs. Implementation of a new matrix diagonalization algorithm[6], due to Pulay, has shown it to be four times faster than the ICEPAK program. Together with improvements in the Davidon-Fletcher-Powell method used for geometry optimization, and various other improvements in our computer programs, these changes have reduced the time required for MNDO calculations by a factor of three. We have also amalgamated our programs for locating transition states, for calculating force constants and vibration frequencies, and for estimating thermodynamic properties from the latter, with the basic MINDO/3 and MNDO programs into a single package and in addition simplified the input. This package should soon be available from QCPE. We have already supplied it to the Air Force Academy and other DOD laboratories. We have also implemented a series of graphics programs, written by Dr. David Pensak at du Pont de Nemours Co. and Capt. Donald Storck at the Air Force Academy, for the display and plotting of molecules in various formats.

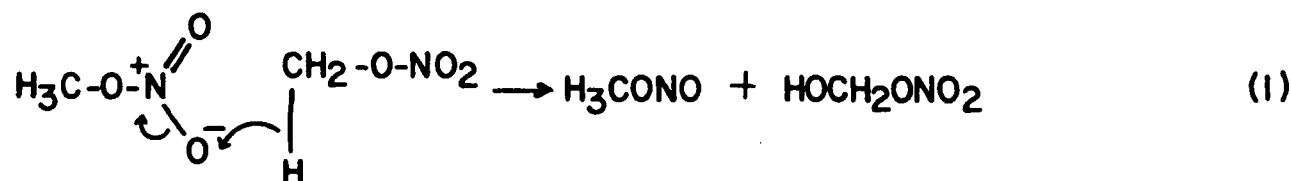
APPLICATIONS TO CHEMICAL PROBLEMS

The rest of the work carried out during the current grant period has been concerned with applications of our procedures to a wide variety of problems of scientific and/or technological interest. A brief summary follows.

A. Initiation of Detonation in Explosives

We completed the study, initiated during the previous grant period, of mechanisms of initiation of detonation in organic explosives containing the NO_2 group.

(a) We confirmed[7] earlier work by Dr. J. Alster, at Picatinny Arsenal, which indicated that the preferred mode of initiation in the detonation of methyl nitrate (1), and so by inference in other nitrate explosives, is an unprecedented insertion of an oxygen atom from one molecule of 1 into a CH bond of another; viz.



The calculated activation parameters, and volume of activation, indicate that this reaction should be 10^7 times faster than fission into radicals ($\text{CH}_3\text{O} + \text{NO}_2$) under the conditions of a detonation shock wave. Bimolecular reactions had not previously been considered as possible candidates for initiation of detonation. This kind of reaction may also be involved in cases where nitro compounds act as oxidizing agents.

(b) The observed activation energies for thermal decomposition of nitromethane (2) and methyl nitrite (3) are significantly less than the energies required to bring about fission into radicals ($\text{CH}_3 + \text{NO}_2$ or $\text{CH}_3\text{O} + \text{NO}$). MINDO/3 calculations[7] indicate that the decomposition of 2 takes place most easily via a preliminary rearrangement to 3 and that the easiest route for decomposition of 3 is by intramolecular elimination of HNO ; i.e.



(2)

2

3

Calculations have also been carried out for the nitroethylenes and nitroacetylenes. Rearrangement of one nitro group in each of these to nitrite is predicted to take place much more easily than that of 2 to 3. The rearrangements are moreover facilitated by nitro groups at the other end of the multiple bond. The activation energies for the rearrangements of tetranitroethylene (4) and dinitroacetylene (5) are consequently very small (<25 kcal/mole). It therefore seems unlikely that either will be stable at room temperature, let alone at higher temperatures. This conclusion places obvious restrictions on possible synthetic routes to these potentially interesting species.

This work was reported at a NATO meeting at Corfu, Greece in, July 1980; at a joint workshop sponsored by AFOSR, ONR, and ARO at Berkeley, California, in January, 1981; and at a meeting organized by ARO at Hilton Head, South Carolina, in April, 1981. A full[7] account is being submitted for publication (JACS).

E Properties of Nitrocubanes

Dr. Alster, at Picatinny Arsenal, has argued convincingly that octanitrocubane (6) should be the "ultimate" conventional explosive, combining high density with a phenomenal energy release per gram. Any organic chemist would, however, have grave doubts concerning its stability.

The decomposition of cubane (7) undoubtedly takes place in a stepwise manner, formation of the biradical (8) being the rate determining step, because any process involving the synchronous breaking of two or more bonds would be "forbidden". Since nitro groups usually seem to stabilize radicals, introduction of nitro groups into 7 might have been expected to facilitate cleavage to 8 and hence the rate of its overall decomposition, probably to the extent of making it dangerously unstable. Our MINDO/3 calculations reproduced the expected mechanism for decomposition of 7 and led to a reasonable estimate (35 kcal/mole) of the activation energy. Very unexpectedly, however, they

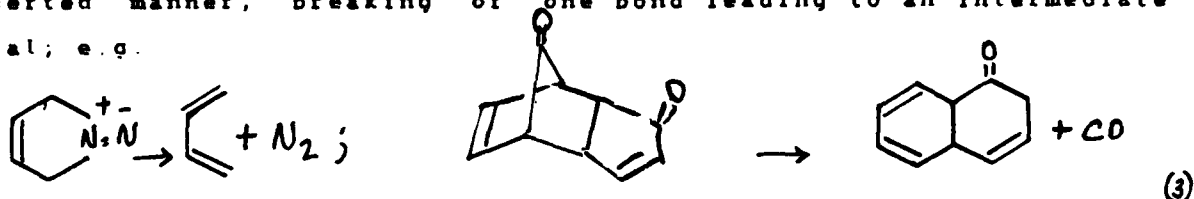
also led to the conclusion that nitro groups should stabilize 7. Introduction of nitro groups at the end of the breaking CC bond raised the activation energy very significantly, suggesting that 6 will probably prove stable enough to be of practical value. This work, which was also reported at the meeting at Hilton Head, has made attempts to prepare 6 a high priority project.

C Chemical Storage of Energy

There is considerable interest in the possible use of thermally reversible photochemical reactions for the storage of solar energy, the photochemical reaction being endothermic so that its subsequent reversal liberates the energy so stored. Most of the work in this area has centered on norbornadiene (9) which, by triplet excitation, is converted to quadricyclene (10). The reverse reaction is exothermic by >20 kcal/mole. The conversion of 9 to 10 requires, however, light of wavelength <300 nm, which comprises only 1% of the solar spectrum, and only a small part of the incident light energy is recovered in the subsequent regeneration of 9. Attempts to improve the performance of 9 by introducing substituents have proved too unpromising to justify the cost of further experimental work. The methods we have developed should prove especially valuable in this kind of situation because calculations for reactions can be carried out very quickly and at a minute fraction of the cost of an experimental study and because the results given by MINDO/3 or MNDO are good enough to serve as a guide to experiment by directing it into promising lines. An extensive MNDO study of the effects of substituents led to the unexpected conclusion that fluorine should exert an especially beneficial effect, the tetrafluoro derivative (11) of 9 being predicted to absorb at longer wavelengths than 9 while the exothermicity of the reverse reaction (12 \rightarrow 11) is 50% greater. While synthesis of 11 would present difficulties, the perfluoro derivative (12) of 9 was predicted to be almost as good and should be easily obtainable from 9 by addition of chlorine, fluorination, and dechlorination. An account of this work has been submitted to JACS[8].

D Mechanisms of Cycloadditions

MINDO/3 and MNDO calculations have been carried out for a variety of reverse chelotropic reactions involving loss of CO or N₂; see Table 1. All cases but one of the reactions were predicted to take place in a nonconcerted manner, breaking of one bond leading to an intermediate biradical; e.g.



Similar conclusions were reached in an earlier MINDO/3 study of the Diels-Alder reaction between ethylene and butadiene and the same has now also been found in a detailed investigation, using both MINDO/3 and MNDO, of the Diels-Alder reactions between maleic anhydride (13) and furan (14a), 2-methylfuran (14b), and 2,5-dimethylfuran (14c). The calculated heats and entropies of activation for all these reactions were in acceptable agreement with experiment. While there are reasons for believing that MINDO/3 and MNDO exaggerate the asymmetry of reactions of this kind where two bonds are predicted to break (or form) at different stages in a reaction, the prediction that such reactions are not synchronous seems very strong.

The only exception found as yet is the chelotropic conversion of the bicyclic diazene (15) to benzene and nitrogen. This, however, was also exceptional in that the calculated activation energy was very small (ca 2 kcal/mole).

Two papers[9,10] reporting this work have been submitted to JACS.

E A New Rule Restricting Reaction Mechanisms.

The work summarized above supports a conclusion drawn from our earlier very extensive studies of pericyclic reactions, that reactions of two-bond type, i.e. reactions involving the making or breaking of two bonds, do not normally take place in a synchronous manner. This new rule can be rationalized in terms of the Evans-Polanyi treatment of transition states and it is consistent with all the available experimental evidence. The only exceptions are reactions involving migration of hydrogen, which are exceptional because of the exceptional propensity of hydrogen to form three-center bonds, and reactions where

the activation energy of the synchronous process is so low that no advantage can be gained from staggering the bond making/breaking processes (e.g. the decomposition of 15). A full account[11] has been submitted to JACS.

F Orbital Isomerism in Radicals.

Some years ago Dewar and Narayanaswami[8] pointed out that the cyclo carbene (16), formed by loss of N_2 from 17, might be expected to exist in two singlet forms of comparable stability, one the true carbene (16) and the other a biradical (18) formed by transfer of a lone pair electron into an empty π MO. 16 and 18 are distinct species, not components of a resonance hybrid, because their wave functions differ in symmetry.

Skeell and his collaborators [12] have presented evidence for isomerism of this kind in amido (19) and acyloxy (20) radicals where the unpaired electron can occupy either a σ or a π MO. We have now studied[13] a number of radicals of this kind, using MNDO, with results in full accord with the experimental evidence. Amido and imido radicals are predicted to exist in the π form, the isomers lying ca 15 kcal/mole higher in energy, whereas the σ forms of acyloxy radicals are predicted to be the most stable. The σ acyloxy radicals are predicted to be unsymmetrical (of 20), as intuition would suggest. An apparent recent claim[14] to the contrary, based on a "state-of-the-art" $ab initio$ calculation, proves on inspection to be meaningless because the radicals were assumed to be symmetrical. Our calculations also provided an intriguing explanation of e.s.r. evidence[12] that the benzoyloxy radical (21) is a radical but has a symmetrical structure. MINDO/3 predicts the σ and π isomers of 21 to have similar energies, so interconversion of the two isomers via the symmetrical isomer could be rapid even at the low temperatures used in the ESR study.

G Photolysis and Thermolysis of Perpropionolactone

While thermolysis of derivatives of per α -pionolactone (22) gives exclusively carbonyl compounds (22 \rightarrow 23), photolysis also gives oxiranes (cf. 24). These results were interpreted[15] in terms of orbital isomerism (see F above) in the intermediate biradicals (cf. 25), it being assumed that the thermal reaction leads to π radicals where decarboxylation is (genuinely) symmetry forbidden whereas photolysis leads to excited σ radicals that lose CO₂ easily, the resulting biradicals (26) cyclizing immediately to oxiranes. The π radicals can, however, undergo a concerted rearrangement and loss of CO₂, conversion of the biradical into normal closed shell molecules acting as the driving force for decarboxylation.

This mechanism is inconsistent with the experiment evidence and theoretical calculations (see F) which indicate that the ground states of acyloxy radicals are the isomers, the isomers being the high energy forms. We have now studied the thermolysis and photolysis of the parent compound, 22, in detail, using MINDO/3 and MNDO. Both reactions start with the formation of the biradical (25) as its gauche isomer (27). This can undergo either internal rotation to the more stable trans isomer (28), or loss of CO₂ concerted with hydrogen migration to form (23), or loss of CO₂ to form 26 and hence 24. 24 can also be formed in one step from 28 by concerted elimination-cyclization. The easiest mode of decomposition of 25 is the second, accounting for the formation of carbonyl compounds in the thermal reaction. The formation of 24 in the photolysis can be attributed either to a "hot molecule" process, the extra energy allowing direct loss of CO₂, or alternatively a triplet state of 25 may be involved, in which case the second mode of decomposition would be inhibited since it would lead to triplet excited 24. Rearrangement of triplet 27 to the more stable trans form (28) would then lead, via singlet 27, to 24.

This work has extensive implications concerning photochemical reactions in general and also indicated the potential usefulness of our procedures for the study of excited state processes. A full account[16] has been submitted for publication (JACS).

H Rearrangement of Cyclohexa-2,5-dienones.

The photochemical rearrangements of derivatives of cyclohexa-2,5-dienone (29) to bicyclo[3,1,0]hexenones (30) has been studied in detail by Zimmerman who interpreted them in terms of an initial cyclization of the $n-\pi^*$ excited state of the dienone to a biradical (31) followed by depromotion of a electron into the singly occupied oxygen AO. The resulting zwitterion rearranges to the product (30). Detailed MINDO/3 calculations now indicate that a $\pi-\pi^*$ excited state is in fact involved, this cyclizing to an orbital isomer of 31 in which the oxygen lone pairs are intact. This work, which has wide implications in organic photochemistry, is in course of publication.

I The Isomeric Benzyne

Some years ago MINDO/3 calculations here[17] led to the unexpected conclusions that m-benzyne (32) should be as stable as the more usual o-benzyne (33), existing in the cyclized form (34), and that a similar bicyclic isomer (35) of p-benzyne should be a local minimum on the C_H potential surface. These predictions were shortly afterwards confirmed by experiment[18,19]. MNDO calculations[20] have now supported and extended these conclusions and also confirmed the suggestion[21] that rearrangements of hexa-3-ene-1,5-dynes (e.g. 36 \rightarrow 37) take place via p-benzyne as an intermediate.

J Claimed Rearrangements of Phenyl Cation

Hehre et al[22], and Speranza[23], have interpreted certain reactions in the gas phase in terms of 1,2 hydrogen shifts in phenyl cation (38). MINDO/3 calculations, however, predict this rearrangement to have a very large activation energy (44 kcal/mole). The matter is of some importance because analogous rearrangements of aryl cations have been postulated from time to time in other connections and because MINDO/3 has so far proven generally reliable in calculations for a wide variety of carbocations. We have now carried out a detailed MINDO/3 study[27] of reactions which might provide alternative explanations of the experimental data, finding them to be viable. There is therefore no reason to doubt the prediction that hydrogen shifts in aryl cations are in fact very difficult.

J The C_H Potential Surface

A detailed MINDO/3 study[28] of the C₄H₄ potential surface led to the location of no less than nineteen minima corresponding to stable species with relatively low energies, together with the transition states for their interconversions. No other potential surface of this degree of complexity has ever been studied in such detail. Apart from being something of a tour de force in the theoretical area, this work is significant in showing how rich and complex potential surfaces may be, even when only a few atoms are involved. Our results emphasize the uselessness of current ab initio methods for studies of this kind, required for the reliable prediction of reactions and their mechanisms. Our MINDO/3 study took ca 1000 hours of central processor time on a CDC 6600 computer. Any ab initio method of comparable performance would have required ca 1000 times as long.

The results are also of general interest because many of the minima corresponded to molecules of very unusual types, implying the presence of unusual kinds of multicenter bonding. This work should stimulate synthetic studies which might open up new areas of organic chemistry. Our calculations also indicated that tetrahedrane (39) should be stable with respect to dissociation into acetylene but that it should rearrange easily to cyclobutadiene (40). These conclusions agree with the results of recent ab initio[26] and MNDO[27] calculations and by the recent preparation[28] of the tetra-*t*-butyl derivative of 39 and the observation[28] that it rearranges easily to the corresponding derivative of 40.

Another conclusion from our calculations is that acetylene should dimerize easily to a carbene (41) which could clearly act as an excellent initiator for polymerization. This provides a satisfying explanation of the fact that acetylene detonates easily, but only under pressure or as a liquid. Initiation of polymerization involves the reaction of 41 with another molecule of acetylene and therefore competes with the unimolecular conversion of 41 to 40 at higher concentrations of the acetylene.

K Sigmaconjugation
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The fact that the conventional strain energies of cyclopropane (42) and cyclobutane (43) are almost the same, in spite of the enormously greater angle strain in the former, has defied description in terms of current organic chemical theory. It has now been pointed out[31] that this is an expected consequence of a fact long known but ignored, i.e. that the resonance integral between two hybrid AOs of a given atom does not vanish, even though the AOs are orthogonal. The CC  $\sigma$  bonds in a paraffin consequently interact with their neighbors just like the CC  $\pi$  bonds in a conjugated polyene. This analogy suggests that such sigmaconjugation in cycloparaffins should have consequences similar to that of normal (pi)conjugation in cyclic polyenes, cycloparaffins thus exhibiting aromaticity if there are  $(4n+2)$  electrons in the CC bonds in the ring and antiaromaticity if there are  $4n$ . The recognition that 42 is in fact sigmaaromatic, being isoconjugate with benzene, accounts for its unexpected stability compared with 43 and also for a number of other anomalies in its behaviour, for example the shortness ( $1.51 \text{ \AA}$ ) of the CC bonds in it and the appearance of its proton NMR signal upfield by 1.1 ppm relative to paraffinic methylene. Sigmaconjugation also accounts for a number of other phenomena that have been difficult to explain in terms of current theory, e.g. the the pyramidal structure of t-butyl radical and the bent structure of triplet carbene. Other phenomena explained nicely in this way include the gauche effect, the anomeric effect, and through-bond coupling between orbitals. A treatment of chelotropic reactions in terms of sigmaconjugation also demonstrates the complete analogy between them and other cycloadditions, making it unnecessary to treat chelotropic reactions as an independent class. A preliminary account of this work has appeared in print[29] while a more detailed one is being submitted to JACS.

#### L Mutual Conjugation in Radicals and Cations

Thirty years ago, in the papers[30] introducing PMO theory, one of the topics treated was the possibility of interactions between substituents attached to a common conjugated system, leading to synergism of their substituent effects. It was shown that such synergism should occur only when one substituent is of -E (electron donating electromeric) and the other of +E (electron accepting



electromeric) type and when the substituents are attached to positions appropriately related to one another. In particular, substituents in an even alternant conjugated system must be attached to positions of opposite parity[30], one starred and one unstarred, while in an odd alternant radical (the only odd system treated) both substituents must be attached to positions that are active[30]. Diphenylpicrylhydrazyl (44) was cited as an example. The term mutual conjugation was suggested for the phenomenon as a whole. Mutual conjugation in even systems had been recognized and interpreted in terms of resonance theory but no convincing explanation can be given in such terms of mutual conjugation in odd alternant systems.

In recent years the latter effect has been "rediscovered" by two groups[32] who have suggested alternative names (merostabilization,<sup>32a</sup> captodative effect<sup>32bc</sup>) for the phenomenon, giving an inevitably inadequate resonance interpretation. A new and better derivation has now been found[33] in terms of PMO theory[30], which moreover leads to the unexpected conclusion that the effect should be even more prominent in odd alternant cations than in the corresponding radicals. Detailed MNDO calculations[33] have confirmed this prediction which should have wide implications in the chemistry of such species.

#### M Biomimetic Cyclizations.

Sterols and triterpenes are now known to be formed in vivo by multiple cyclizations of open chain polyenes, each ring being formed by intramolecular addition of a carbocation to a C=C bond, the result being another carbocation which in turn can attack another C=C bond. This kind of reaction has found extensive use in synthesis and is now commonly described as biomimetic cyclization. Doubt remains, however, concerning its mechanism. In particular, in the case of multiple cyclizations, there has been much discussion concerning the timing of the various steps. The fact that addition to each C=C bond takes place stereospecifically trans has been taken as evidence for a fully synchronous mechanism. The stereochemistry of such reactions can, however, be explained in terms of a stepwise mechanism if the addition of each cation to a C=C bond leads to a  $\pi$  complex[34] rather than a classical carbonium ion. This possibility has been undervalued because

of the failure of many organic chemists, including those working in this area, to accept the complex theory.

We have now studied this problem by carrying out detailed calculations for the double cyclization of cis (45) and trans (46) 2-undeca-6,10-dienyl cation to cis and trans methyltetralinyl cations (47). The reactions were found to take place in steps, via complexes (e.g. 48) as stable intermediates, with consequent[34] stereospecific trans addition to the C=C bond. There now seems little doubt that similar complex mechanisms will be found for other biomimetic cyclizations. A paper[35] reporting this work has been submitted to JACS.

#### N Benzene Dication.

Recent experimental work has suggested that derivatives of the benzene dication exist as "nonclassical" pyramidal structures (49), analogous to the isoelectronic pyramidal carborane,  $C_2B_4H_6$  (50). Detailed MINDO/3 calculations have confirmed that the pyramidal structures for such ions are minima on the relevant potential energy surfaces but have also led to the prediction that the isomeric "classical" structures (51) should be comparable in stability. A number of ions of this kind, derived from substituted benzenes, have been studied, using MINDO/3, and the activation energies for interconversion of the isomers, 50 and 51, determined. Another problem of interest is the multiplicity of the ground states of these dications. Hexachlorobenzene dication has been reported to have a triplet ground state. Our calculations are in agreement with this observation but suggest that benzene dication itself should be a singlet. This work, which has suggested a number of promising experimental studies, is in course of publication[36].

#### O Reactions of Singlet Dioxygen

The mechanism of reactions of singlet ( $\overset{1}{A}$ ) oxygen ( $O_2$ ) with olefins remains the subject of controversy. MINDO/3 calculations[37] suggested some years ago that the first step is the formation of a peroxirane (e.g. 52), but Goddard et al[38] have claimed on the basis of CVB calculations that biradicals such as 53 are lower in energy

than the isomeric peroxiranes. Stephenson[39] has shown that such biradicals cannot in fact be involved in these reactions and all the experimental evidence can indeed be explained convincingly in terms of peroxirane intermediates. Further support for this has now been provided by a detailed MINDO/3 study of the peroxiranes that can be derived from singlet oxygen and limonene (54). The products from this reaction have been analyzed in detail[40], experimentally. The calculations provide a wholly satisfactory interpretation of the experimental results. This work is being submitted for publication in JACS.

#### P Refutation of the Frontier Orbital Method.

The frontier orbital method has attracted a considerable following in recent years in spite of its obvious and familiar theoretical deficiencies, presumably on the grounds that whatever these may be, it nevertheless works in practice. Attention is drawn in a paper, about to be submitted to JACS, of an exception extreme enough to throw doubt on the whole FO approach.

All theoretical treatments so far tried, now including MNDO, agree in concluding that the frontier orbital density in 10,9-borazarophenanthrene (55) at the 9-position is the least, or almost the least, at any position and certainly the least at any CH group. According to frontier orbital theory, this should then be the least reactive position in the whole molecule to electrophilic attack. In practice[46], however, it is the most reactive of all! The frontier orbital density at the second most reactive position (6; see 55) is also less than at a number of other less reactive positions.

The frontier orbital method is generally satisfactory only in the case of alternant hydrocarbons and then only because of a coincidental correspondence between frontier orbital coefficients and localization energies that was pointed out many years ago. Since there are no problems that cannot be treated more simply and more effectively in terms of the PMO method than in terms of the frontier orbital method and since the former is both more reliable and better founded in theory, it would seem high time that the whole frontier orbital approach was pensioned off, if not exterminated.

## Q Carboranes

A very detailed MNDO study of the carboranes has been reported[39], covering all the compounds that have been prepared or postulated as well as a number of others. The results were in good general agreement with experiment and led to apparently reasonable interpretations of the experimental data in several places where there has been controversy.

## R Why Are Large Conjugated Aromatic Rings Aromatic?

It has been taken for granted for many years that Hückel's rules apply to conjugated rings of all sizes and for the same reasons, i.e. the specific resonance stabilization in rings containing  $(4n+2)$  electrons. Calculations here over the years, by progressively more sophisticated parametric methods, have, however, agreed in incorrectly predicting bonds to alternate in length even in cyclic polyenes of quite moderate size; for example in Boekelheide's [14]annulene derivative (56) and even in azulene (57). We have assumed in the past that this represented a weakness of ZDO procedures. However Haddon[40] has now found the same to be true for ab initio calculations using the STO-3G and 4-31G basis sets.

It occurred to us that the equalization of bond lengths might in fact be due not to the aromaticity of these compounds but to an unusual kind of electron correlation. In a cyclic polyene, the number of electrons is equal to the number of bonds. There will therefore be a tendency for electrons of opposite spins to segregate themselves in alternate bonds and thus to make all the bonds in the ring equivalent. This cannot happen in an open chain polyene because the number of bonds is then one less than the number of electrons. This would account nicely for the fact that bond lengths in open chain polyenes alternate strongly whereas those in aromatic rings do not, even when the rings are very large. This picture is of course similar to Lowdin's alternant orbital model, which, however, considered alternation of electrons only between atoms, not bonds. We have checked this suggestion by carrying out spin-unrestricted (UHF) MNDO calculations[41] for a number of large ring systems, with results in very good agreement with experiment. Since the alternation effect should hold equally for  $4n$  and  $(4n+2)$  rings, it may well be that the larger  $4n$  polyenes will prove to have

equal bond lengths since the effects of antiaromaticity are expected to decrease with ring size.

#### 8 Other Topics Studied.

A number of other topics have been studied, the investigations being at various stages.

(a) MNDO calculations for beryllium-indenyl and fluorenyl complexes[42] were carried out as models for the iron tricarbonyl complexes,  $\text{BeH}^+$  and  $\text{Fe}(\text{CO})_3^+$  being analogous in their ability to bring three ligands. The results agree with experimental data for the latter.

(b) A detailed comparison[43] of the results of MINDO/3 calculations for a variety of open shell systems, using the generalized SCF coupling operator and "half-electron" methods, led, as expected, to similar results, thus justifying use of the "half-electron" method, which is simpler.

(c) A program was written for MNDO calculations for linear polymers, using the tight binding approximation, and used to calculate the geometry, vibration frequencies, and electrical properties of polyethylene and polyperdeuterioethylene. The results agreed with experiment[44].

(d) Calculations for a wide variety of haloolefins led to a satisfying explanation of observations at Allied Corp. concerning their retention on glo columns[45].

(e) MNDO calculations for the allyl and crotyl anions, and for their  $\text{BeH}$  derivatives (studied as models of their lithium derivatives, parameters for lithium being unavailable), led to results in agreement with the available experimental evidence and provided satisfactory explanations of it[46].

(f) MNDO calculations have been used to assign ultraviolet photoelectron (UPE) spectra of phenoxy radical[47] and other aryloxy radicals and also to show that the UPE spectrum measured for what was assumed to be phenylchlorocarbene (58) in fact corresponded to a mixture of the chlorocycloheptatrienocarbenes, e.g. 59, formed by rearrangement of 59.

(g) MNDO calculations were also used to interpret the upe spectra of various derivatives of t-butylacetylene[48].

(h) MNDO calculations of the vibrational spectra of a variety of boron compounds agreed with experiment where experimental data were available and also led to various predictions[49].

(i) Calculations[50] of the ionization energies of p-quinodimethane (60a) and its 2,5-dimethyl derivative (60b) led to a reassignment of their UPE spectra, contradicting a claim to have observed "shake-up" bands.

(j) Calculations for the reactions of carbon atoms with carbonyl compounds led to a reinterpretation of the experimental results reported by Shevlin, which was subsequently confirmed by Shevlin as a result of experiments suggested by our calculations[51].

(k) MNDO calculations[52,53] were used to assign the UPE spectra of phenylphosphine and a number of its derivatives, with results in disagreement with the previously accepted assignment. The new assignments were confirmed by experimental studies suggested by the calculations.

(l) Calculations for a number of reactions of very simple systems, e.g. the rearrangement of vinylidene ( $\text{H}_2\text{C}=\text{C}::$ ) to acetylene, agreed gratifyingly well with those from high level ab initio calculations[56]. In our opinion the main chemical value of the latter lies in their possible provision of data needed to calibrate of parametric procedures such as ours. A paper reporting this work is in preparation.

(m) In the same vein, MINDO/3 calculations have been carried out for the ethane dication ( $\text{C}_2\text{H}_2^{++}$ ). The results agree with those from a recent high level ab initio calculation, predicting the most stable form to be the diborane analog, (61), and predicting an isomeric structure (62) to be a second minimum on the potential surface. However, MINDO/3 also predicted the existence of another stable isomer, i.e. 63.

(n) Calculations for  $S_7$  have shown it to occur in two distinct isomeric forms, one with a boat (64) geometry and one a chair (65). While each isomer undergoes pseudorotation without activation, the isomers are separated by an appreciable energy barrier. This work was carried out in collaboration with Dr. E. Wasserman, at the Central Research Laboratories of du Pont de Nemours Co., and will be published jointly in a paper reporting his experimental studies in this area.

The following received financial support under Contract 79-0008

Michael J.S. Dewar

Bonnie George

James Ritchie

Lynnette Bounds

Tze-Pei Tien

Don David

George Ford

James Friedheim

Lek Chantranupong

Charles Reynolds

James Stewart

Maria Belen Rodriguez

James Neece

Suzanne Quarry

Kathryn Whites

Francisco Carrion



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- (48) Publications - 475
- (49) Publications - 472
- (50) Publications - 478
- (51) Publications - 473
- (52) Publications - 474
- (53) Publications - 475

MANUSCRIPTS ACCEPTED FOR PUBLICATION

MICHAEL J.S.DEWAR

- A1. J. Comput. Chem. "Ground States of Molecules 56. MNDO  
Calculations for Molecules Containing Sulfur", Dewar, McKee.
- A2. J. Comput. Chem. "Ground States of Molecules 53. MNDO  
Calculations for Molecules Containing Chlorine", Dewar,  
Rzepa.
- A3. J.A.C.S. "Ground States of Molecules 61. "Relative  
Stabilities of O-, M-, and P-Benzynes". Dewar, Ford, Rzepa,  
Reynolds.
- A4. Organometallic, "Why Life Exists", Dewar.

## MANUSCRIPTS SUBMITTED FOR PUBLICATION

MICHAEL J. S. DEWAR

- B1. J.A.C.S. "Energy Storage by Norbornadiene Derivatives",  
Dewar Pakiari.
- B2. J.A.C.S. "The (CR)<sub>6</sub> System", Dewar, Holloway, Nelson.
- B3. J.A.C.S. "Photolysis and Thermolysis  
of  $\gamma$ -Perpropionolactone" Dewar, Pakiari.
- B4. J.A.C.S. "Ground States of Molecules. 62. Reverse  
Chelotropic Reactions in Polycyclic Systems", Dewar,  
Chantranupong.
- B5. J.A.C.S. "Ground States of Molecules. 63. MINDO/3 and MNDO  
Studies of Some Chelotropic Reactions", Dewar,  
Chantranupong.
- B6. J.A.C.S. "Mechanism of the Diels-Alder Reaction. Studies  
of the Addition of Maleic Anhydride to Furan and  
Methylfurans", Dewar, Pierini.
- B7. J.A.C.S. "Multi-bond Reactions Cannot Normally Be  
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- B8. J. Comput. Chem. "Ground States of Molecules 64. MNDO  
Calculations for Compounds Containing Bromine", Dewar,  
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- B9. "Proton Migration in Phenyl Cation?". Dewar, Reynolds.

## MANUSCRIPTS IN PROGRESS

MICHAEL J. S. DEWAR

- C1. "Ground States of Molecules. Part 65. S<sub>2</sub> Reactions and Related Processes", Dewar, Carrion.  
N
- C2. "Ground States of Molecules. Part 66. Biomimetic Cyclization", Dewar, Reynolds.
- C3. "Proton Migration in Phenyl Cation?", Dewar, Reynolds.
- C4. "Sigmaconjugation in Radicals, Biradicals, Carbenes, and Transition States; Sigmaaromaticity and the Significance of Hybridization", Dewar.
- C5. "Ground States of Molecules. Part 67. Thermolysis of Molecules Containing NO<sub>2</sub> Groups", Dewar, Ritchie.  
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- C7. "MNDO Calculations for Molecules Containing Iodine". Dewar, Healy.
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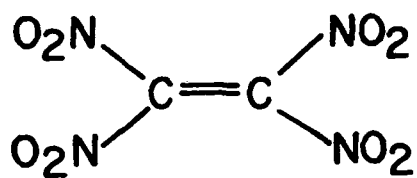


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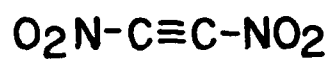
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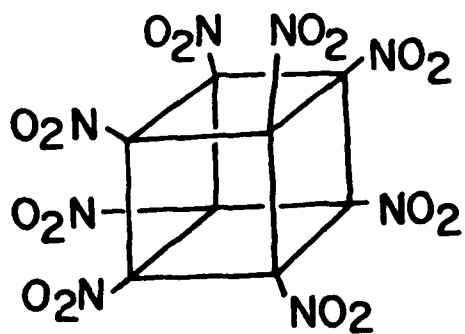
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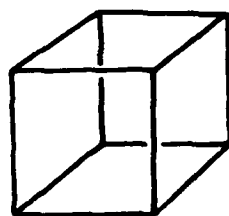
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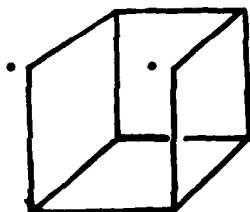
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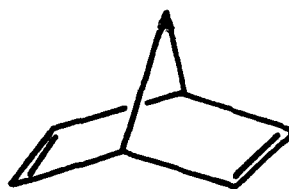
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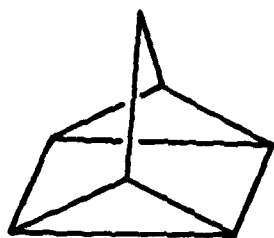
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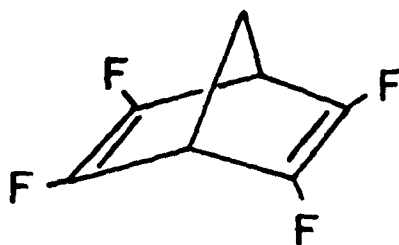
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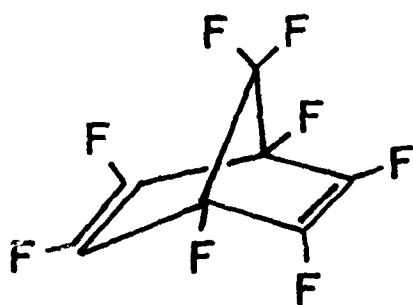
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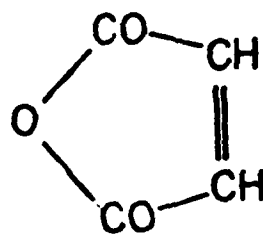
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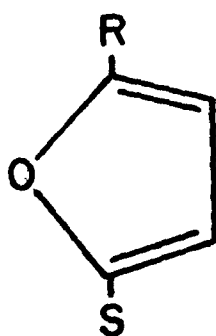
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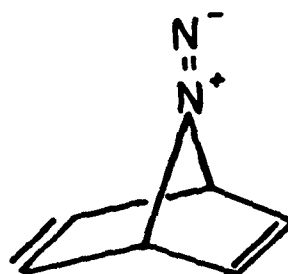
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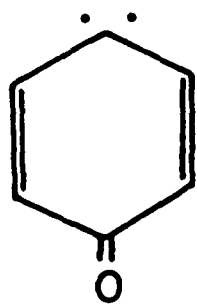
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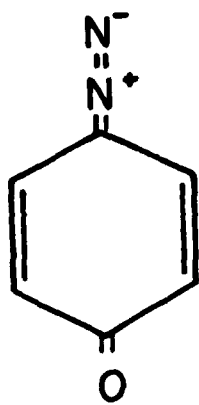
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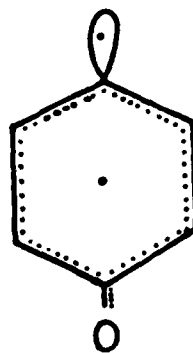
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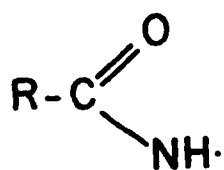
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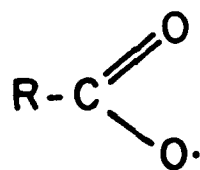
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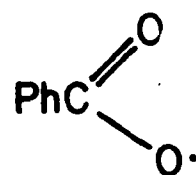
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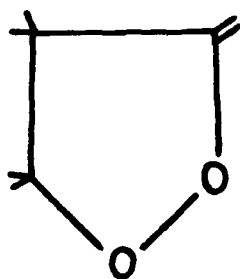
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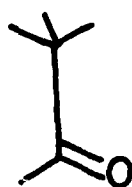
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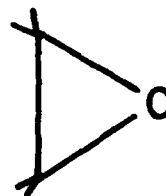
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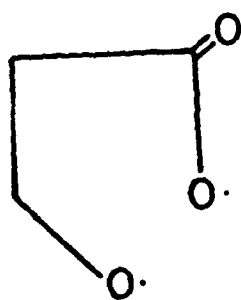
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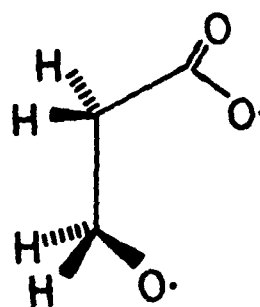
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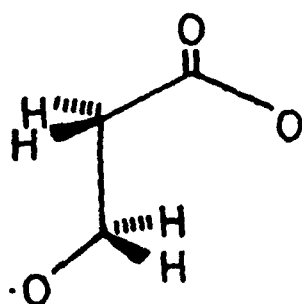
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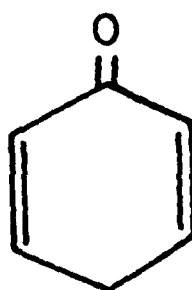
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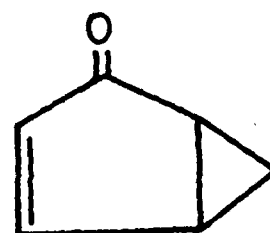
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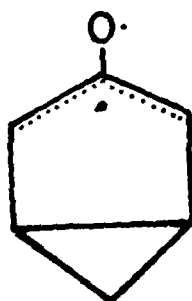
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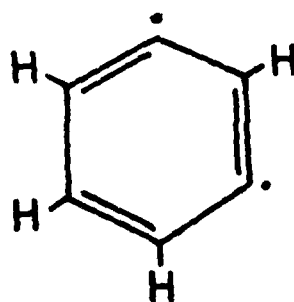
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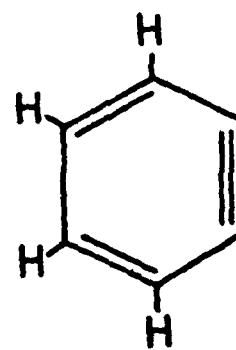
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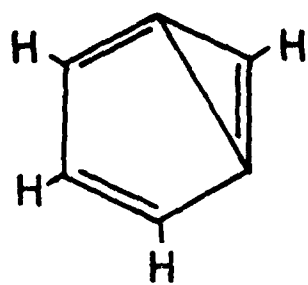
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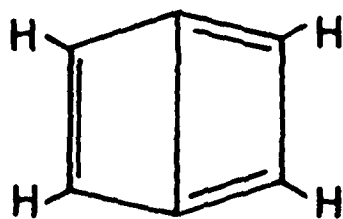
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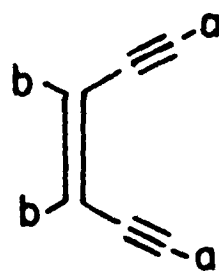
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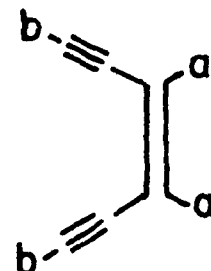
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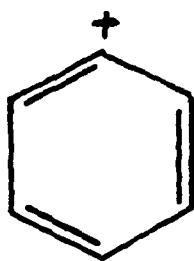
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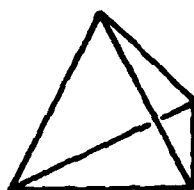
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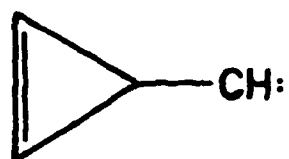
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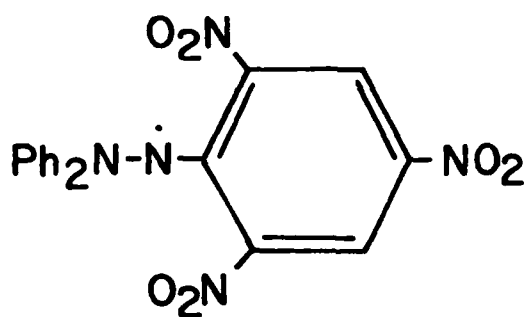
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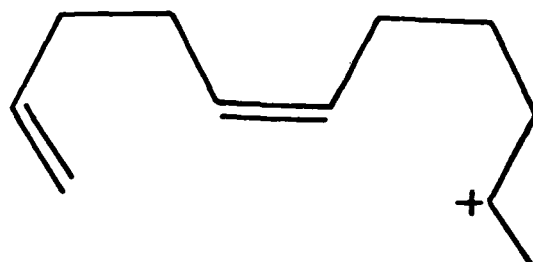
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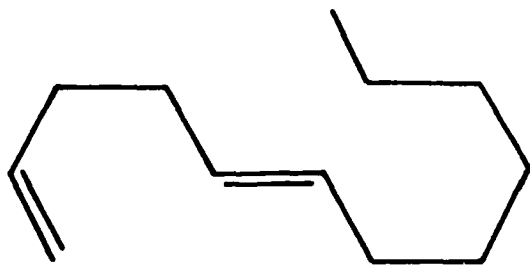
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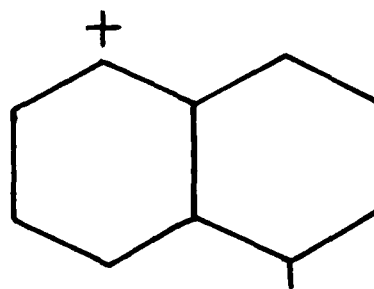
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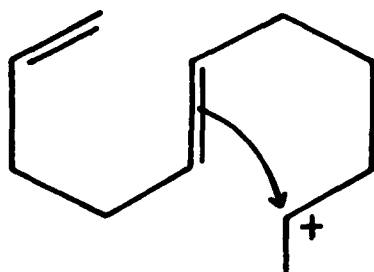
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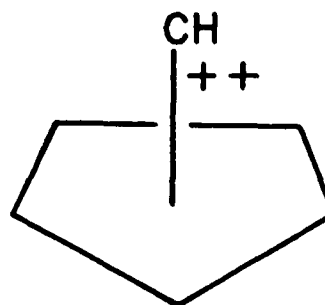
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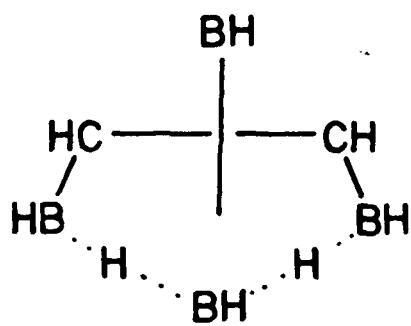


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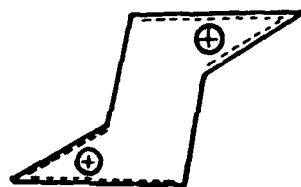


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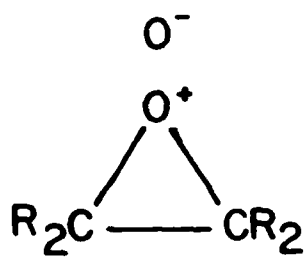




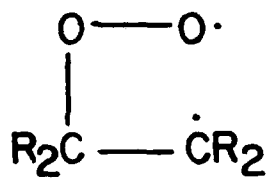
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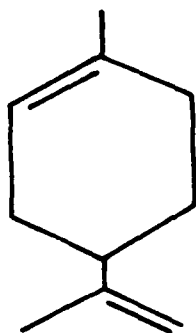
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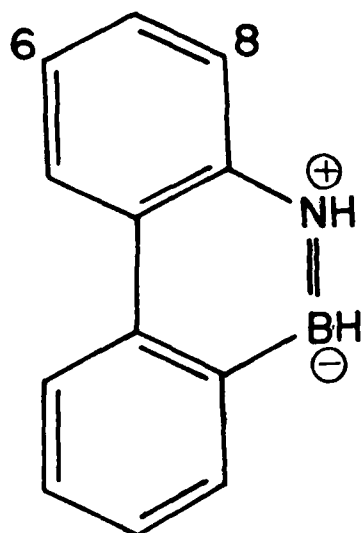
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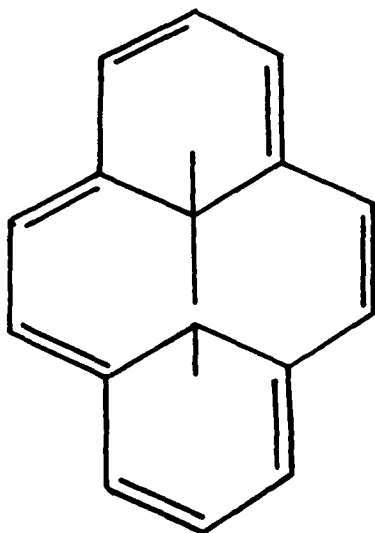
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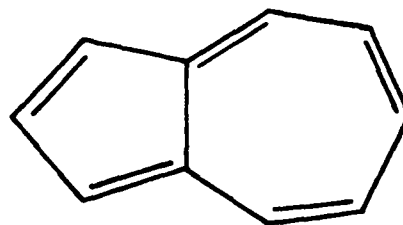
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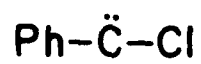
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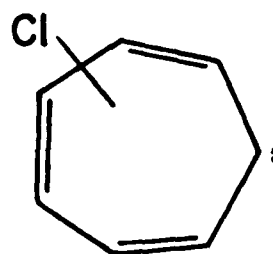
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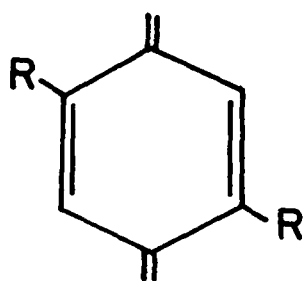
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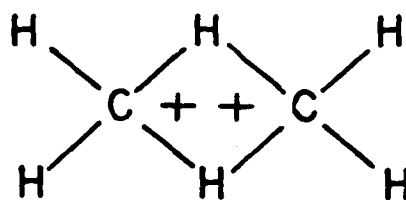
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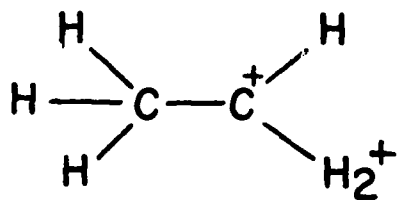
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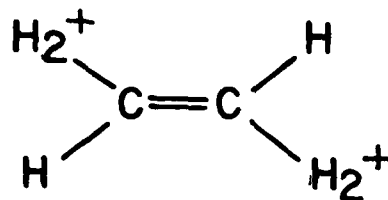
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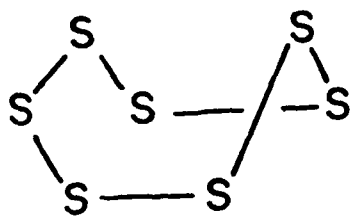
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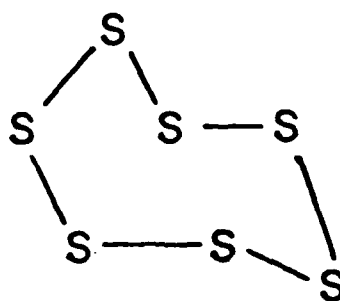
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